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| (54) Title: PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS (57) Abstract A personal care composition comprising: (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises: (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a T _g of from about -120 °C to about 25 °C and (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a T _g of from above about 25 °C to about 250 °C wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and (b) a personal care carrier. | | |

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PERSONAL CARE COMPOSITIONS CONTAINING LINEAR TOUGHENED SILICONE GRAFTED POLYMERS

TECHNICAL FIELD

The present invention relates to personal care compositions, such as haircare, cosmetic and nail compositions containing linear toughened silicone grafted polymers.

BACKGROUND OF THE INVENTION

Cosmetic compositions such as lotions, creams, emulsions, packs, make-up (e.g., foundations, lipsticks, eye shadows and the like) and hair compositions are used to improve one's outward appearance. Many personal care products use contain various resins, gums, and adhesive polymers. The polymers are used for a variety of purposes including thickening, feel properties, film-forming ability, active deposition, active penetration, hair holding, etc. Consequently there is constantly a search for developing polymers having improved properties for use in personal care product. Many of these compositions require the use of adhesive silicone grafted polymers. For example, the desire to have the hair retain a particular shape is widely held. The most common methodology for accomplishing this is the application of a styling composition to dampened hair, after shampooing and/or conditioning, or to dry, styled hair. These compositions provide temporary setting benefits and they can be removed by water or by shampooing. The materials used in the compositions to provide the setting benefits have generally been resins and have been applied in the form of mousses, gels, lotions or sprays.

Many people desire a high level of style retention, or hold, from a hair spray composition. In typical hair sprays, hold is achieved by the use of resins, such as AMPHOMER^R, supplied by National Starch and Chemical Company, and GANTREZ^R SP 225, supplied by GAF. In general, as hair hold for hair spray compositions is increased, the tactile

feel of the hair becomes stiffer and hence, less desirable. It is desirable to provide hair spray products which could provide an improved combination of hair hold and hair feel characteristics.

Recently, it has become known to utilize silicone grafted organic backbone polymers in various personal care compositions including their use as hair setting agents in hairspray compositions and other hair styling compositions, e.g. hair tonics, lotions, rinses, mousses, etc. Silicone grafted polymers can be used to make personal care compositions with improved feel, e.g., in the case of hair sprays, increased softness relative to conventional polymeric hair setting agents.

However, it remains desirable to improve the performance of these silicone grafted polymers. It is an object of this invention to provide personal care compositions containing linear toughened silicone graft copolymers.

It is a further object of this invention to provide personal care compositions containing resins that have improved adhesive and cohesive properties thereby providing improved durability benefits (e.g., style benefits).

These and other benefits as may be apparent from the description below can be obtained by the present invention.

The present compositions can comprise, consist of, or consist essentially of any of the required or optional ingredients and/or limitations described herein.

All percentages and ratios are calculated on a weight basis unless otherwise indicated. All percentages are calculated based upon the total composition unless otherwise indicated.

All ingredient levels refer to the active level of that ingredient, and are exclusive of solvents, by-products, or other impurities that may be present in commercially available sources, unless otherwise indicated.

SUMMARY OF THE INVENTION

The present invention relates to a personal care composition comprising:

- (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
 - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
 - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
- (b) a personal care carrier.

DETAILED DESCRIPTION OF THE INVENTION

The essential components of the present invention are described below. Also included is a nonexclusive description of various optional and preferred components useful in embodiments of the present invention.

Silicone Grafted Adhesive Polymer

The compositions according to the invention comprise, as an essential component, a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises:

- (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000. This silicone containing hair styling polymer is preferably colloiddally dispersed or solubilized in any applicable carrier.

The compositions hereof will generally comprise from about 0.1% to about 99%, preferably from 0.5% to about 50%, more preferably from about 1% to about 10%, by weight of the composition, of the silicone grafted polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film or a weld. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The silicone grafted polymers are characterized by polysiloxane moieties covalently bonded to and pendant from a polymeric carbon-based backbone.

The backbone will preferably be a carbon chain derived from polymerization of ethylenically unsaturated monomers. The backbone comprises (a) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and (b) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers,

and/or epoxides) with non-polysiloxane-containing polymerizable monomers.

The polysiloxane-grafted polymer should have a weight average molecular weight of at least about 20,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 3,000,000. Preferably, the weight average molecular weight will be between about 50,000 and about 2,000,000, more preferably between about 75,000 and about 1,000,000, most preferably between about 100,000 and about 750,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about -5°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the polymer, if such a transition exists for a given polymer. Preferably, the Tg is above about -20°C, more preferably above about -5°C. Preferably the adhesive polymer of the present invention has a Tg below about 60°C, more preferably below about 50°C and most preferably below about 40°C.

The silicone grafted polymers for the compositions of the present invention comprise "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

When used in a composition, such as a personal care composition for application to the hair or skin, the non-polysiloxane portion should permit the polymer to deposit on the intended surface, such as hair or skin.

The polysiloxane macromer should have a weight average molecular weight of at least about 1000, preferably from about 1,000 to about 50,000, more preferably from about 5,000 to about 50,000, most preferably about

8,000 to about 25,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc.

The preferred silicone grafted polymers are comprised of monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

Vinyl Monomer Units

The silicone copolymers of the present invention comprise from about 50% to about 98%, preferably from about 60% to about 95%, and more preferably from about 70% to about 90% by weight of the vinyl monomer units.

The vinyl monomer unit is selected from copolymerizable monomers, preferably ethylenically unsaturated monomers. The vinyl monomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the vinyl monomer can be reacted with or polymerized with the polysiloxane macromonomers in a polymerization reaction using one or more conventional synthetic techniques, such as ionic, emulsion, dispersion, Ziegler-Natta, free radical, group transfer or step growth polymerization. In the present invention, monomers and macromonomers that are copolymerizable using conventional free radical initiated techniques are preferred. The term "ethylenically unsaturated" is used herein to mean a material that contains at least one polymerizable carbon-carbon double bond, which can be mono-, di-, tri- or tetra-substituted.

The monomer units can be derived from hydrophilic monomers (typically polar monomers), or mixtures of such hydrophilic monomers with hydrophobic monomers (typically low polarity monomers), provided that the

solubility characteristics of the overall copolymer is achieved. As used herein, "hydrophilic monomers" means monomers which form homopolymers which are substantially water soluble; "hydrophobic monomers" means monomers which form substantially water insoluble homopolymers.

Nonlimiting classes of monomers useful herein include monomers selected from the group consisting of unsaturated alcohols, unsaturated monocarboxylic acids, unsaturated dicarboxylic acids, unsaturated anhydrides, alcohol esters of unsaturated monocarboxylic acids, alcohol esters of unsaturated dicarboxylic acids, alcohol esters of unsaturated anhydrides, alkoxylated esters of unsaturated monocarboxylic acids, alkoxylated esters of unsaturated dicarboxylic acids, alkoxylated esters of unsaturated anhydrides, aminoalkyl esters of unsaturated monocarboxylic acids, aminoalkyl esters of unsaturated dicarboxylic acids, aminoalkyl esters of unsaturated anhydrides, amides of unsaturated monocarboxylic acids, amides of unsaturated dicarboxylic acids, amides of unsaturated anhydrides, salts of unsaturated monocarboxylic acids, salts of unsaturated dicarboxylic acids, salts of unsaturated anhydrides, unsaturated hydrocarbons, unsaturated heterocycles, and mixtures thereof.

Representative examples of such monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), vinyl caprolactam, methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-

1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the number of carbon atoms preferably being from about 1-12; dicyclopentenyl acrylate; 4-biphenyl acrylate; pentachlorophenyl acrylate; 3,5-dimethyladamantyl acrylate; 3,5-dimethyladamentyl methacrylate; 4-methoxycarbonylphenyl methacrylate; trimethylsilyl methacrylate; styrene; alkyl substituted styrenes including alpha-methylstyrene and t-butylstyrene; vinyl esters, including vinyl acetate, vinyl neononanoate, vinyl pivalate and vinyl propionate; vinyl chloride; vinylidene chloride; vinyl toluene; alkyl vinyl ethers, including isobutyl vinyl ether and s-butyl vinyl ether; butadiene; cyclohexadiene; bicycloheptadiene; 2,3-dicarboxylmethyl-1,6-hexadiene; ethylene; propylene; indene; norbornylene; β -pinene; α -pinene; salts of acids and amines listed above, and combinations thereof. The quaternized monomers can be quaternized either before or after the copolymerization with other monomers of the graft copolymer.

Preferred monomers include acrylic acid, methacrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, styrene, alpha-methylstyrene, t-butylstyrene, vinyl acetate, vinyl propionate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, salts of any acids and amines listed above, and mixtures thereof.

From the above descriptions, esters of acrylic and methacrylic acid that form low T_g homopolymers include, for example, 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl

ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, isobutyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate; Acrylamide monomers including N-dodecylacrylamide, N-octadecylacrylamide; Vinyl monomers including sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether and Styrene monomers including 4-decylstyrene. Other monomers that form low Tg homopolymers include isobutylene, 1-butene, 5-methyl-1-hexene, olefinic monomers that could be hydrogenated post polymerization (after formation of copolymers), for example, isoprene, 1,2-butadiene, 1,4-butadiene.

Preferred monomers which form low Tg homopolymers include 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide.

Most Preferred monomers which form low Tg homopolymers include 2-methoxyethyl acrylate, n-butyl acrylate, ethyl acrylate. These low Tg monomers preferably have Tg of from about -70°C to about 25°C, more preferably from about -60°C to about 0°C and most preferably from about -60°C to about -20°C.

From the above descriptions, acrylic and methacrylic acids that form high Tg homopolymers include, for example, sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamentyl methacrylate,

isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate (silyl esters could be hydrolysed to form acrylic or methacrylic acids), acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids; Acrylamide & methacrylamide monomers including N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide; Vinyl monomers including: 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole; Styrene monomers including: styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate. Other monomers that form high Tg homopolymers include: diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl styrene, α -methyl styrene, indene, norbornene, norbornylene.

Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene, α -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide.

Most Preferred monomers which form high Tg homopolymers include: t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene. These high Tg monomers preferably have Tg of from above about 25° C to about 250° C, more preferably from about 30° C to about 200° C, even more preferably from about 35° C to about 150° C, and most preferably from about 40° C to about 130° C.

Polysiloxane Macromonomer Units

The copolymers of the present invention comprise from about 2% to about 50%, preferably from about 5% to about 40%, and more preferably from about 10% to about 30%, by weight of the copolymer of polysiloxane macromonomer units.

The polysiloxane macromonomer units are copolymerizable with the vinyl monomers, said macromonomers preferably having a vinyl moiety. Either a single type of macromonomer unit or combinations of two or more macromonomer units can be utilized herein. The macromonomers are selected to meet the requirements of the copolymer. By "copolymerizable", as used herein, is meant that the macromonomers can be reacted with or polymerized with the vinyl monomers in a polymerization reaction using one or more conventional synthetic techniques, as described above.

The polysiloxane macromonomers that are useful herein contain a polymeric portion and a copolymerizable moiety which is preferably an ethylenically unsaturated moiety. Typically, the preferred macromonomers are those that are endcapped with the vinyl moiety. By "endcapped" as used herein is meant that the vinyl moiety is at or near a terminal position of the macromonomer.

The macromonomers can be synthesized utilizing a variety of standard synthetic procedures familiar to the polymer chemist of ordinary skill in the art. Furthermore, these macromonomers can be synthesized starting from commercially available polymers. Typically, the weight average molecular weight of the macromonomer is from about 1000 to about 50,000.

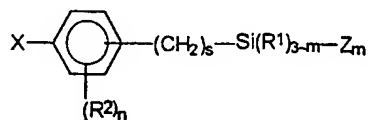
Polysiloxane macromonomers are exemplified by the general formula:



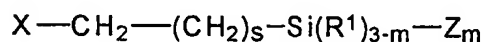
wherein X is a vinyl group copolymerizable with the vinyl monomer units; Y is a divalent linking group; each R is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. The polysiloxane macromonomer has a weight average molecular weight from

about 1000 to about 50,000, preferably from about 5,000 to about 30,000, more preferably from about 8,000 to about 25,000.

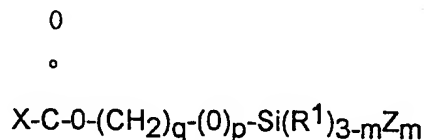
Preferably, the polysiloxane macromonomer has a formula selected from the following formulas:



or

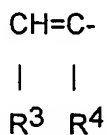


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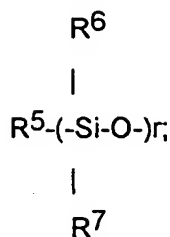


In these structures s is an integer from 0 to 6; preferably 0, 1, or 2; more preferably 0 or 1; m is an integer from 1 to 3, preferably 1; p is 0 or 1; q is an integer from 2 to 6; each R^1 is independently selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, preferably C1-C6 alkyl, or C1-C6 alkyl or alkoxy-substituted phenyl, more preferably C1-C6 alkyl, even more preferably methyl, R^2 is selected from the group consisting of C1-C6 alkyl or C1-C6 alkyl substituted phenyl, preferably methyl.

n is an integer from 0 to 4, preferably 0 or 1, more preferably 0; X is



wherein R^3 is hydrogen or $-\text{COOH}$, preferably R^3 is hydrogen; R^4 is hydrogen, methyl or $-\text{CH}_2\text{COOH}$, preferably R^4 is methyl; Z is



wherein R^5 , R^6 , and R^7 , are independently selected from hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alkyl or alkoxy-substituted phenyl, hydrogen or hydroxyl, preferably R^5 , R^6 , and R^7 are C1-C6 alkyls; more preferably methyl; and r is an integer of from about 14 to about 700, preferably about 60 to about 400, and more preferably about 100 to about 350.

Exemplary silicone grafted polymers for use in the present invention include the following, where the composition is given as weight part of monomer used in the synthesis:

- (i) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)
 MWt of copolymer: 210,000
 Composition: t-butyl acrylate (36%), n-butyl acrylate (27%), acrylic acid (12%), methacrylic acid (10%), poly(dimethylsiloxane) (15%)
 MWt of poly(dimethylsiloxane): 10,000
- (ii) poly(t-butyl acrylate-co-ethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)
 MWt of copolymer: 100,000
 Composition: t-butyl acrylate (34%), ethyl acrylate (35%), acrylic acid (21%), poly(dimethylsiloxane) (10%)
 MWt of poly(dimethylsiloxane): 5,000
- (iii) poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 150,000

Composition: t-butyl acrylate (47.25%), n-butyl acrylate (22.75%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

- (iv) poly(t-butyl acrylate-co-2-methoxyethyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 100,000

Composition: t-butyl acrylate (27%), 2-methoxyethyl acrylate (43%), methacrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

- (v) poly(t-butyl acrylate-co-isobornyl acrylate-co-2-methoxyethyl acrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 95,000

Composition: t-butyl acrylate (33%), isobornyl acrylate (17%), 2-methoxyethyl acrylate (20%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 10,000

- (vi) poly(t-butyl acrylate-co-lauryl methacrylate-co-acrylic acid)-graft-poly(dimethylsiloxane)

MWt of copolymer: 125,000

Composition: t-butyl acrylate (60%), lauryl methacrylate (10%), acrylic acid (20%), poly(dimethylsiloxane) (10%)

MWt of poly(dimethylsiloxane): 15,000

The Tg's for monomer units above can be found in The Polymer Handbook, third edition, (John Wiley & Sons, 1989) and the backbone Tg can be calculated using the method illustrated in Fundamental Principles of Polymeric Materials, second edition (John Wiley & Sons, 1993). Representative Tg's for monomers in the exemplary silicone grafted

polymers described above are as follows: The Tg of t-butyl acrylate is 44.85°C; the Tg of n-butyl acrylate is -54.15°C; the Tg of acrylic acid is 105.85°C; the Tg of methacrylic acid is 227.85°C; the Tg of ethyl acrylate is -24.15°C; the Tg of lauryl methacrylate is -65.15°C; and the Tg of 2-methoxyethyl acrylate is -50.15°C.

The silicone grafted polymers can be synthesized by free radical polymerization of the polysiloxane-containing monomers with the non-polysiloxane-containing monomers. The synthetic procedures are in general the same as those described for the adhesive copolymer. The silicone macromer is added in to the reactor along with the "A" and "B" monomers, and the reaction proceeds as for the adhesive copolymer examples. Compared to the adhesive copolymer, it may be necessary to choose different solvents for the polymerization reaction, as apparent to one skilled in the art, to keep the monomers and polymers in solution throughout the polymerization.

Without being limited by theory, it is believed that in forming the above-described silicone grafted polymers, there is some polymer which does not incorporate the silicone graft; such polymers have a relatively low weight average molecular weight e.g., below 20,000.

Personal Care Carrier

The compositions of the present invention comprise from about 0.1% to about 99.9%, preferably from about 0.5% to about 99.0% and most preferably from about 1.0% to about 99.9% of a suitable personal care carrier. Suitable carriers are fully described in U.S. Patent 5,061,481 issued October 29, 1991 to Suzuki et al., incorporated by reference herein. For example, skin care carriers typically comprise oil-in-water emulsions.

Hair spray compositions typically comprise a polar solvent phase as a liquid vehicle for the silicone grafted polymer. The polar solvent phases comprise one or more polar solvents that are present in the hair care compositions at a level of from about 80% to about 99%, preferably from

about 85% to about 98%, more preferably from about 90% to about 95% of the total composition.

The polar solvents essential to the present compositions are selected from the group consisting of water, C₂-C₃ monohydric alkanols, and mixtures thereof. If present, C₃ alkanols, such as isopropanol, should be used at levels no greater than about 15% by weight of the composition, preferably no greater than about 12%, more preferably no greater than about 10%. High levels of C₃ monohydric alcohols are undesirable in the present compositions due to potential odor issues they can create. Preferred polar solvent phases contain water, ethanol, or mixtures thereof.

Where water and alcohol mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the alcohol solvents are generally present in the range of from 0.5% to about 99%, preferably from about 50% to about 95%, by weight of the total composition.

In yet another aspect of this invention are provided hair styling products, such as hair spray compositions, which contain reduced levels of volatile organic solvents. A reduced volatile organic solvent hair spray composition of the present invention contains no more than 80% volatile organic solvents (which include, for example, alkanols but not water). As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the reduced volatile organic solvent hair styling products hereof, the compositions generally comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water.

The reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up

to about 60% even more preferably no more than about 50%, water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvent. It is also contemplated that the compositions can be limited to containing no more than about 75%, 65%, 55%, or other levels of volatile organic solvents.

Shampoos and rinse compositions typically comprise a volatile, nonpolar, branched chain hydrocarbon and is safe for topical application to the skin and hair. The branched chain hydrocarbon solvent hereof is present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 2% to about 8%, by weight of the composition. Also useful are low boiling point silicone oils.

The branched chain hydrocarbon solvent is characterized by a boiling point of at least about 105°C, preferably at least about 110°C, more preferably at least about 125°C, most preferably at least about 150°C. The boiling point is also generally about 260°C or less, preferably about 200°C or less. The hydrocarbon chosen should also be safe for topical application to the hair and skin.

The branched chain hydrocarbon solvents are selected from the group consisting of C₁₀-C₁₄ branched chain hydrocarbons, and mixtures thereof, preferably C₁₁-C₁₃ branched chain hydrocarbons, more preferably C₁₂ branched chain hydrocarbons. Saturated hydrocarbons are preferred, although it isn't necessarily intended to exclude unsaturated hydrocarbons.

Examples of suitable nonpolar solvents include isoparaffins of the above chain sizes. Isoparaffins are commercially available from Exxon Chemical Co. Examples include IsoparTM G (C₁₀-C₁₁ isoparaffins), IsoparTM H and K (C₁₁-C₁₂ isoparaffins), and IsoparTM L (C₁₁-C₁₃ isoparaffins). The most preferred nonpolar solvent are C₁₂ branched chain hydrocarbons, especially isododecane. Isododecane is commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as PermethylTM 99A.

Plasticizer

The compositions hereof can optionally contain a plasticizer for the silicone grafted polymer. Any plasticizer suitable for use in hair care products or for topical application to the hair or skin can be used. A wide variety of plasticizers are known in the art. These include acetyl triethylcitrate, triethylcitrate, glycerin, diisobutyl adipate, butyl stearate, and propylene glycol. Plasticizers are typically used at levels of from about 0.01% to about 10%, by weight of the composition, preferably from about 0.05% to about 3%, more preferably from about 0.05% to about 1%.

Optional Components

Adhesive Polymer

The compositions of the present invention can comprise an additional adhesive polymer. The compositions hereof will generally comprise from about 0.1% to about 15%, preferably from 0.5% to about 8%, more preferably from about 1% to about 8%, by weight of the composition, of the adhesive polymer. It is not intended to exclude the use of higher or lower levels of the polymers, as long as an effective amount is used to provide adhesive or film-forming properties to the composition and the composition can be formulated and effectively applied for its intended purpose. By adhesive polymer what is meant is that when applied as a solution to a surface and dried, the polymer forms a film. Such a film will have adhesive and cohesive strength, as is understood by those skilled in the art.

The polymeric backbone is chosen such that it is compatible with the silicone adhesive styling polymer. By "compatible" is meant is that, when placed in a suitable solvent, the polymers form a stable solution, i. e., the polymers do not compete for solubility and therefore, cause no phase separation and when the solution is dried a uniform film is formed, with no macrophase separation of the two polymers. A suitable solvent is a solvent which substantially completely dissolves the non-silicone and silicone grafted polymers at the levels described herein. The polymer blend forms a relatively clear hairspray system (% transmittance at 450 nm is generally

greater than 80%). It is recognized that certain plasticizers can form cloudy films as well as incorrect neutralization levels. Therefore, this would fall outside this definition of compatibility. The compatibility can be tested by dissolving the adhesive polymer and the silicone grafted hair styling resin in a mutual solvent, and then evaporating the solvent to form a film. Incompatible polymers will form a cloudy film with poor mechanical properties, due to the large scale phase separation of the two polymers. Alternatively, after drying the polymer solution to a film, compatibility can be evaluated by measuring the Tg. Compatible polymers will have a single Tg, while incompatible polymers will exhibit two Tg's. Although compatibility can occur between two polymers of completely different structures, it is preferred that compatibility be obtained by making the composition of the non-silicone backbone of the silicone grafted polymer similar to or identical to the composition of the adhesive polymer.

The adhesive polymer should have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

Preferably, the adhesive hereof when dried to form a film have a Tg of at least about -20°C, more preferably at least about 20°C, so that they are not unduly sticky, or "tacky" to the touch. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the backbone of the

polymer. Preferably, the Tg is above about -20°C, more preferably above about 20°C.

Preferably the weight ratio of the non-silicone polymer to silicone grafted polymer ranges from about 1:10 to about 1:1, preferably from about 1:5 to about 1:1.

Exemplary adhesive polymers for use in the present invention include the following, where the numbers following the structure indicate the weight ratios of monomers as loaded into the polymerization reactor:

- (i) acrylic acid/t-butyl acrylate 25/75
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate 40/40/20
- (iii) t-butylacrylate/acrylic acid 65/35
- (iv) polymer (ii) quaternized by treatment with methyl chloride

The adhesive polymers can be synthesized as described above such as by free radical polymerization of the monomers.

Solubility of the adhesive polymer, as described above, should be determined after neutralization, if any, as well as after addition of other ingredients that may be included in the polar solvent phase, such as surfactants, solubilizers, etc.

The present compositions can contain a wide variety of additional optional ingredients, including among them any of the types of ingredients known in the art for use in hair setting compositions, especially hair spray compositions and hair setting tonics. These ingredients include, but are not limited to, surfactants (including fluorinated surfactants and silicone copolyols), and ionic strength modifiers, propellants, hair conditioning agents (e.g., silicone fluids, fatty esters, fatty alcohols, long chain hydrocarbons, cationic surfactants, etc.)

Ionic Strength Modifier System

Optionally, the compositions of the present invention can contain an effective amount of a non-surface active ionic strength modifier system for reducing the viscosity of the hair spray composition. When used, the ionic

strength modifiers will be present in the present compositions at a level of at least about 0.01%, by weight of the composition. The upper limit is dependent upon the maximum amount of the ionic strength modifiers that can be present in the particular compositions hereof such that the hair setting resin remains solubilized or dispersed. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the resin will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the polar liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, resin, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched chain organic heterochain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus, basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof

are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in

the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The use of ionic strength modifiers are especially useful in reduced volatile organic solvent compositions, most especially those utilizing silicone macromer-containing polymers.

Personal Care Compositions

The present invention encompasses a wide variety of personal care compositions, including shampoos, soaps, lotions, creams, antiperspirants, nail enamels, lipsticks, foundations, mascaras, sunscreens, hair spray compositions, mousses, and hair setting tonics. Compositions that will be flowable, e.g., low viscosity compositions that, preferably, are suitable for spray application as well as higher viscosity compositions are also contemplated.

Personal care carriers are suitable for use in the present invention are described in U.S. Patent 5,306,485 to Robinson et al., issued April 26, 1994, and U.S. Patent 5,002,680 to Schmidt et al., issued March 26, 1991, both of which are incorporated by reference herein. Hair spray compositions and mousses of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquefied lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are

hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, N-butane, isobutane, propanes, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas and mixtures thereof.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 40% by weight of the total composition.

Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from American National Can Corp.

Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other hair styling compositions include tonics and lotions, which are typically dispensed in a conventional bottle or tube, and applied directly to the hair or first dispensed to the hand and then to the hair.

The hair styling formulations of the present invention can optionally contain conventional hair care composition adjuvants. Generally, adjuvants

collectively can comprise from about 0.05% to about 5% by weight and preferably from about 0.1% to about 3%, by weight. Such conventional optional adjuvants are well known to those skilled in the art and include in addition to those discussed above, emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints, bleaches, reducing agents and other colorants; pH adjusting agents sunscreens; preservatives; thickening agents (e.g. polymeric thickeners, such as xanthan gum); and perfume.

METHOD OF MAKING

The personal care compositions of the present invention can be made using conventional formulation and mixing techniques.

METHOD OF USE

The compositions of the present invention are used in conventional ways to provide the personal care compositions of the present invention. Such method generally involves application of an effective amount of the product. For example, in a hair spray composition, said composition is applied to the desired dry, slightly damp, or wet hair before and/or after the hair is arranged to a desired style. The composition is then dried or allowed to dry. By "effective amount" is meant an amount sufficient to provide the desired benefits.

The following Experimentals and Examples further illustrate embodiments within the scope of the present invention. They are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXPERIMENTALS

The following synthesis exemplify silicone grafted polymers useful in the present compositions.

Polymer 1

Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Place 42.75 parts of t-butyl acrylate, 27.25 parts n-butyl acrylate, 10 parts methacrylic acid, 10 parts acrylic acid, and 10 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

Polymer 2

Synthesis of Poly(t-butyl acrylate-co-n-butyl acrylate-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Place 32 parts of t-butyl acrylate, 27 parts n-butyl acrylate, 21 parts methacrylic acid, and 20 parts polydimethylsiloxane macromonomer in a roundbottom flask. Add sufficient acetone as the reaction solvent to produce a final monomer concentration of 20%. Purge the vessel with argon for approximately one hour. Following the purge, maintain a constant positive pressure on the closed reaction system with argon. Heat the reaction to 58°C. Prepare a 10% solution of azobisisobutyronitrile (0.5% by weight relative to the amount of monomer) in acetone, and add it to the reaction mixture. Maintain heat and stirring for 20 hours. Terminate the

reaction by opening the reactor to atmosphere and cooling to room temperature.

The polymer solution is then precipitated in water at one part solution to 15 parts water. The resultant polymer is then redissolved in acetone. This procedure is repeated six times, with the final polymer being placed in a vacuum oven for heated drying. This completes the polymer purification process.

EXAMPLES

Examples 1-4

The following examples represent nonaerosol hairspray compositions of the present invention.

| | <u>Example No</u> | | | |
|-------------------------------|-------------------|-------|-------|-------|
| Component (wt. %) | 1 | 2 | 3 | 4 |
| Copolymer ¹ | 4.00 | 4.75 | 5.50 | 5.50 |
| Isododecane ² | 1.00 | 1.00 | 1.00 | 3.00 |
| Diisopropyl butyl adipate | 0.40 | 0.75 | 0.90 | 0.55 |
| Sodium hydroxide ³ | 0.96 | 1.20 | 1.44 | 1.6 |
| Perfume | 0.10 | 0.10 | 0.10 | 0.10 |
| Water | 17.00 | 20.00 | 20.00 | 18.00 |
| Ethanol ⁴ | 76.54 | 71.95 | 70.56 | 71.25 |

¹ Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane).

² PERMETHYL 99A, from Presperse, Inc., South Plainfield, NJ, USA.

³ Sodium hydroxide is 30% active.

⁴ SDA 40 (100% ethanol).

EXAMPLE 5Sunscreen Composition

An oil-in-water emulsion is prepared by combining the following components utilizing conventional mixing techniques.

Ingredients

| <u>Phase A</u> | <u>Weight %</u> |
|----------------|-----------------|
|----------------|-----------------|

| | |
|------------------|-------|
| Water | QS100 |
| Carbomer 954[1] | 0.24 |
| Carbomer 1342[2] | 0.16 |
| Copolymer[3] | 1.00 |
| Disodium EDTA | 0.05 |

Phase B

| | |
|-------------------------------|------|
| Isoarachidyl Neopentanoate[4] | 2.00 |
| PVP Eicosene Copolymer[5] | 2.00 |
| Octyl Methoxycinnamate | 7.50 |
| Octocrylene | 4.00 |
| Oxybenzone | 1.00 |
| Titanium Dioxide | 2.00 |
| Cetyl Palmitate | 0.75 |
| Stearoxytrimethylsilane (and) | |
| Stearyl Alcohol[6] | 0.50 |
| Glyceryl Tribehenate | 0.75 |
| Dimethicone | 1.00 |
| Tocopheryl Acetate | 0.10 |
| DEA-Cetyl Phosphate | 0.20 |

Phase C

| | |
|---------------------|------|
| Water | 2.00 |
| Triethanolamine 99% | 0.60 |
| NaOH solution 40% | 0.33 |

Phase D

| | |
|-------|------|
| Water | 2.00 |
|-------|------|

| | |
|--|------|
| Butylene Glycol | 2.00 |
| DMDM Hydantoin (and) | |
| Iodopropynyl Butylcarbamate ^[7] | 0.25 |
| dL Panthenol | 1.00 |
| <u>Phase E</u> | |
| dimethylmyristamine | 0.36 |

- [1] Available as Carbopol® 954 from B.F. Goodrich.
- [2] Available as Carbopol® 1342 from B.F. Goodrich.
- [3] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)
- [4] Available as Ganex V-220 from GAF Corporation.
- [5] Available as DC 580 Wax from Dow Corning.
- [6] Available as Synchrowax HRC from Croda.
- [7] Available as Glydant Plus from Lonza.

In a suitable vessel the Phase A ingredients are dispersed in the water and heated to 75-85°C. In a separate vessel the Phase B ingredients (except DEA-Cetyl Phosphate) are combined and heated to 85-90°C until melted. Next, the DEA-Cetyl Phosphate is added to the liquid Phase B and stirred until dissolved. This mixture is then added to Phase A to form the emulsion. The Phase C ingredients are combined until dissolved and then added to the emulsion. The emulsion is then cooled to 40-45°C with continued mixing. In another vessel, the Phase D ingredients are heated with mixing to 40-45°C until a clear solution is formed and this solution is then added to the emulsion. Finally, the emulsion is cooled to 35°C and the Phase E ingredients are combined at 65°C, use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Phase E is the cooled to 35°C, added and mixed.

This emulsion is useful for topical application to the skin to provide protection from the harmful effects of ultraviolet radiation.

EXAMPLE 6Facial Moisturizer

A leave-on facial emulsion composition containing a cationic hydrophobic surfactant is prepared by combining the following components utilizing conventional mixing techniques.

| <u>Ingredient</u> | <u>Weight %</u> |
|---------------------------------|-----------------|
| Phase A | |
| Water | QS100 |
| Glycerin | 3.00 |
| Cetyl Palmitate | 3.00 |
| Cetyl Alcohol | 1.26 |
| Quaternium-22 | 1.00 |
| Glyceryl Monohydroxy Stearate | 0.74 |
| Dimethicone | 0.60 |
| Stearic Acid | 0.55 |
| Octyldodecyl Myristate | 0.30 |
| Potassium Hydroxide | 0.20 |
| Carbomer 1342 | 0.125 |
| Tetrasodium EDTA | 0.10 |
| DMDM Hydantoin and Iodopropynyl | |
| Butyl Carbamate | 0.10 |
| Carbomer 951 | 0.075 |
| Phase B | |
| Isododecane | 4.00 |
| Copolymer ^[1] | 1.00 |
| stearamine | 0.36 |

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

In a suitable vessel the Phase A ingredients are combined to form an emulsion. Phase B is prepared by dispersing the copolymer in Isododecane (solvent) then adding the stearamine. Heat the solution to 65°C and use an

appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Cool the Phase B and mix into Phase A using conventional mixing techniques.

This emulsion is useful for application to the skin as a moisturizer.

EXAMPLE 7

The following is an anti-perspirant composition representative of the present invention.

| Component | Weight % |
|---|----------|
| PPG 2 Myristyl Propionate | 34.00 % |
| Glyceryl C ₁₈ - C ₃₆ Wax Acid Ester | 0.40 % |
| Cyclomethicone | 32.75 % |
| Copolymer[1] | 1.00 % |
| dimethylmyristamine | 0.50 % |
| Aluminum Chlorohydrate | 19.00 % |
| PPG 5 Ceteth 20 | 7.50 % |
| Water | 1.50 % |

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

Mix PPG 2 Myristyl Propionate and Glyceryl C₁₈ - C₃₆ Wax Acid Ester, heat to 75°C. Disperse the Chlorohydrate. Disperse the copolymer in Cyclomethicone (solvent) then add the dimethylmyristamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. Add the cyclomethicone mixture to the Chlorohydrate dispersion. Mix PPG 5 Ceteth 20 and the water, the add to oils, perfume and cool.

EXAMPLE 8

The following is an anti-acne composition representative of the present invention.

| Component | Weight % |
|------------------------------|---------------|
| <u>Copolymer-Solvent Mix</u> | |
| Copolymer[1] | 1.00 % |
| dimethylpalmitamine | 0.18 % |
| Isopar H® [2] | 3.75 % |
| <u>Main Mix</u> | |
| Water | Q.S. to 100 % |
| Ethanol (SDA 40) | 40.00 % |
| Carbopol 940® | 0.75 % |
| Triethanol Amine | 1.00 % |
| Salicylic Acid | 2.00 % |

[1]Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

[2]C₁₁-C₁₂ Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improve water resistance and is useful in the treatment of acne.

EXAMPLE 9

The following is an anti-acne composition representative of the present invention.

| Component | Weight % |
|------------------------------|---------------|
| <u>Copolymer-Solvent Mix</u> | |
| Copolymer[1] | 1.00 % |
| dimethylpalmitamine | 0.18 % |
| Isopar H® [2] | 3.75 % |
| <u>Main Mix</u> | |
| Water | Q.S. to 100 % |
| Ethanol (SDA 40) | 20.00 % |
| Carbopol 940® | 0.75 % |
| Triethanol Amine | 1.00 % |
| Ibuprofen | 2.00 % |

[1] Poly(t-butyl acrylate-co-n-butyl acrylate-co-acrylic acid-co-methacrylic acid)-graft-poly(dimethylsiloxane)

[2] C₁₁-C₁₂ Isoparaffin, available from Exxon Chemical Co.

This product is prepared by dispersing the copolymer in Isopar H® (solvent) then adding the dimethylpalmitamine. Heat the solution to 65°C and use an appropriate homogenizer to facilitate incorporation of the copolymer into the solvent. The other components are mixed in a separate vessel at ambient temperature. The copolymer-solvent premix is cooled (if needed) and added to the other components. This composition is useful for application to the skin to provide improve water resistance and is useful for the analgesic effects.

WHAT IS CLAIMED IS:

1. A personal care composition comprising:
 - (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
 - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and
 - (ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25°C to about 250°Cwherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and
 - (b) a personal care carrier.
2. A personal care composition according to Claim 1, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C₁-C₁₈ alcohols, styrene; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-

methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above.

3. A personal care composition according to Claim 2 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, 2-phenoxyethyl ester, 2-hydroxyethyl ester, 4-hydroxybutyl acrylate, 2-ethoxyethoxyethyl acrylate, 2-ethoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, n-ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-dodecylacrylamide, N-octadecylacrylamide, sec-butyl vinyl ether, butyl vinyl ether, vinyl propionate, vinyl butyrate, decylvinyl ether, methyl vinyl ether, 4-decylstyrene, isobutylene, 1-butene, 5-methyl-1-hexene, isoprene, 1,2-butadiene, 1,4-butadiene and mixtures thereof.
4. A personal care composition according to Claim 3 wherein the monomer of (a) is selected from the group consisting of 3-methoxybutyl acrylate, 2-methoxyethyl acrylate, n-butyl acrylate, dodecyl acrylate, 2-ethylhexyl acrylate, 2-ethylbutyl acrylate, ethyl acrylate, n-heptyl acrylate, n-hexyl acrylate, iso-butyl acrylate, iso-decyl acrylate, iso-propyl acrylate, 3-methylbutyl acrylate, 2-methylpentyl acrylate, nonyl acrylate, octyl acrylate, 2-ethylhexyl methacrylate, n-pentyl methacrylate, N-octadecylacrylamide and mixtures thereof.

5. A personal care composition according to Claim 4 wherein the monomer of (a) is selected from the group consisting of 2-methoxyethyl acrylate, n-butyl acrylate, n-ethyl acrylate and mixtures thereof.
6. A personal care composition according to Claim 3 wherein the monomer of (a) has a Tg of from about -70° C to about 25° C.
7. A personal care composition according to Claim 6 wherein the monomer of (a) has a Tg of from about -60° C to about 0° C.
8. A personal care composition according to Claim 7 wherein the monomer of (a) has a Tg of from about -60° C to about -20° C.
9. A personal care composition according to Claim 2 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-dimethyladamentyl methacrylate, isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl

styrene, α -methyl styrene, indene, norbornene, norbornylene and mixtures thereof.

10. A personal care composition according to Claim 9 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, dimethyl aminoethyl methacrylate, isopropyl methacrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene, α -methyl styrene, 2-vinylpyridine, 4-vinylpyridine, N-isopropylacrylamide, N-t-butylmethacrylamide and mixtures thereof.
11. A personal care composition according to Claim 10 wherein the monomer of (b) is selected from the group consisting of t-butyl methacrylate, t-butyl acrylate, methyl methacrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, tert-butyl styrene.
12. A personal care composition according to Claim 9 wherein the monomer of (b) has a Tg of from above about 30° C to about 200° C.
13. A personal care composition according to Claim 12 wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.
14. A personal care composition according to Claim 11 wherein the monomer of (b) has a Tg of from about 40° C to about 130° C.

15. A personal care composition according to Claim 4 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
- from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and
 - from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:
$$X(Y)_nSi(R)_{3-m}(Z)_m$$
 wherein:
X is a vinyl group copolymerizable with said vinyl monomer units;
Y is a divalent linking group;
R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;
Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;
n is 0 or 1; and
m is an integer from 1 to 3.
16. A personal care composition according to Claim 8 wherein said copolymer is formed from the random copolymerization of the following relative weight percentages of vinyl monomer units and polysiloxane-containing macromonomer units:
- from about 50% to about 98%, by weight of said copolymer, of vinyl monomer units, and

- b. from about 2% to about 50%, by weight of said copolymer, of polysiloxane-containing macromonomer units, wherein said polysiloxane-containing macromonomer units have a weight average molecular weight from about 1,000 to about 50,000, and correspond to the chemical formula:

$X(Y)_nSi(R)_{3-m}(Z)_m$ wherein:

X is a vinyl group copolymerizable with said vinyl monomer units;

Y is a divalent linking group;

R is selected from the group consisting of hydrogen, hydroxyl, C1-C6 alkyl, C1-C6 alkoxy, C2-C6 alkylamino, phenyl, C1-C6 alky or alkoxy-substituted phenyl;

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 1000, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization;

n is 0 or 1; and

m is an integer from 1 to 3.

17. A personal care composition according to Claim 1 in the form of a shampoo, soap, lotion, cream, antiperspirant, nail enamel, lipstick, foundation, mascara, sunscreen, hair spray, mousse or hair setting tonic.
18. A hairspray composition comprising
- (a) a silicone grafted adhesive polymer, said polymer being characterized by an organic polymeric backbone wherein said backbone comprises
 - (i) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from about -120° C to about 25° C and

(ii) at least one monomer wherein when said monomer is polymerized as a homopolymer having a Tg of from above about 25° C to about 250° C

wherein said silicone grafted adhesive polymer has silicone macromers grafted to said backbone and wherein the number average molecular weight of said silicone macromers is greater than about 1000; and

(b) a solvent carrier.

19. A hairspray composition according to Claim 17, wherein said monomer of (a) and (b) is independently selected from the group consisting of acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, esters of C₁-C₁₈ alcohols, styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene and salts of acids and amines above and wherein the monomer of (a) has a Tg of from about -60° C to about -20° C .
20. A hairspray composition according to Claim 17 wherein the monomer of (b) is selected from the group consisting of sec-butyl methacrylate, t-butyl acrylate, methyl methacrylate, isopropyl methacrylate, 2-t-butylaminoethyl methacrylate, dimethyl aminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, 4-biphenyl acrylate, pentachlorophenyl acrylate, 3,5-dimethyladamantyl acrylate, 3,5-

dimethyladamentyl methacrylate, isobornyl acrylate, trimethylsilyl methacrylate, trimethylsilyl acrylate, acrylic acid, methacrylic acid, salts of acrylic and methacrylic acids, N-butylacrylamide, acrylamide, N-isopropylacrylamide, N-t-butylmethacrylamide, 2-vinylpyridine, 4-vinylpyridine, vinyl acetate, vinyl chloride, N-vinylcaprolactam, N-vinyl pyrrolidone, cyclohexyl vinyl ether, vinyl alcohol, vinyl imidazole, styrene, 4-t-butylstyrene, 2-methoxystyrene, 4-acetylstyrene, styrene sulfonate, diallyldimethylammonium chloride, maleimides, crotonic acid, itaconic acid, maleic anhydrides, allyl alcohol, α -pinene, β -pinene, tert-butyl styrene, α -methyl styrene, indene, norbornene, norbornylene and mixtures thereof and wherein the monomer of (b) has a Tg of from about 35° C to about 150° C.

INTERNATIONAL SEARCH REPORT

International Application

PCT/US 98/08285

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/48 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
| X | EP 0 388 582 A (KOBAYASHI KOSE CO) 26 September 1990 see example 1 --- | 1-20 |
| X | US 4 981 902 A (GARBE JAMES E ET AL) 1 January 1991 see column 11, line 56 - column 12, line 41; claims 1-11 --- | 1-16 |
| X | EP 0 391 273 A (SHIONOGI & CO ;NISSHIN KAGAKU KOGYO KK (JP)) 10 October 1990 see examples --- | 1-17 |
| X | EP 0 408 311 A (MITSUBISHI PETROCHEMICAL CO) 16 January 1991 see examples 3,4 --- | 1-20 |
| | -/-- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-----------------------|
| X | EP 0 769 290 A (OREAL) 23 April 1997 see page 3, line 10 - page 5, line 16 --- | 1-20 |
| X | WO 95 00106 A (PROCTER & GAMBLE :WELCH ROSEMARY JANE (GB); DODSWORTH EMMA LOUISE) 5 January 1995 see claim 8 --- | 1-20 |
| X | WO 93 03705 A (PROCTER & GAMBLE) 4 March 1993 see page 17, line 24-28 ----- | 1-20 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application

PCT/US 98/08285

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0388582 A | 26-09-1990 | JP 2247110 A | 02-10-1990 |
| | | JP 2741237 B | 15-04-1998 |
| | | JP 2250812 A | 08-10-1990 |
| | | JP 2132141 A | 21-05-1990 |
| | | JP 2700816 B | 21-01-1998 |
| | | JP 2258709 A | 19-10-1990 |
| | | JP 2279617 A | 15-11-1990 |
| | | DE 69014358 D | 12-01-1995 |
| | | DE 69014358 T | 14-06-1995 |
| | | US 5061481 A | 29-10-1991 |
| | | US 5219560 A | 15-06-1993 |
| | | JP 3008432 A | 16-01-1991 |
| US 4981902 A | 01-01-1991 | US RE34902 E | 11-04-1995 |
| | | US 4988506 A | 29-01-1991 |
| EP 0391273 A | 10-10-1990 | JP 2262511 A | 25-10-1990 |
| | | JP 2740541 B | 15-04-1998 |
| | | DE 69006242 D | 10-03-1994 |
| | | DE 69006242 T | 05-05-1994 |
| | | DK 391273 T | 28-02-1994 |
| | | ES 2062147 T | 16-12-1994 |
| | | US 5229435 A | 20-07-1993 |
| EP 0408311 A | 16-01-1991 | DE 69028742 D | 07-11-1996 |
| | | JP 3128909 A | 31-05-1991 |
| | | US 5480634 A | 02-01-1996 |
| | | US 5166276 A | 24-11-1992 |
| EP 0769290 A | 23-04-1997 | FR 2739283 A | 04-04-1997 |
| | | JP 9110632 A | 28-04-1997 |
| WO 9500106 A | 05-01-1995 | AU 7200594 A | 17-01-1995 |
| WO 9303705 A | 04-03-1993 | AT 139436 T | 15-07-1996 |
| | | AU 671598 B | 05-09-1996 |
| | | AU 2508592 A | 16-03-1993 |
| | | BR 9206386 A | 13-12-1994 |
| | | CA 2115155 A | 04-03-1993 |
| | | CN 1070334 A | 31-03-1993 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte Jona Application No

PCT/US 98/08285

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO 9303705 A | | CZ 9400351 A | 18-05-1994 |
| | | DE 69211699 D | 25-07-1996 |
| | | DE 69211699 T | 28-11-1996 |
| | | DK 600013 T | 28-10-1996 |
| | | EP 0600013 A | 08-06-1994 |
| | | ES 2088590 T | 16-08-1996 |
| | | FI 940770 A | 18-02-1994 |
| | | GR 3020298 T | 30-09-1996 |
| | | HU 67309 A | 28-03-1995 |
| | | JP 6509808 T | 02-11-1994 |
| | | MX 9204801 A | 01-04-1993 |
| | | NO 940537 A | 18-04-1994 |
| | | NZ 243995 A | 28-08-1995 |
| | | PT 100790 A | 30-09-1993 |
| | | SK 19394 A | 09-11-1994 |

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